Electrolytic nickel recovery from lithium-ion batteries ☆

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Abstract

Lithium/cobalt/nickel oxide ($LiCo_xNi_{1-x}O_2$, $0 < x < 1$) is one of the cathode materials currently used in commercial Li-ion batteries. The direct Ni recovery by electrochemical methods from leach liquor obtained by dissolution of this cathode is not possible because of cobalt anomalous co-deposition.

After separating Ni from Co by SX methods, nickel has been recovered by means of both galvanostatic and potentiostatic electrowinning. Operative conditions such as solution pH, temperature, Ni concentration, bath agitation and, in the case of galvanostatic operation, current density have been determined for the selected cathode and anode material.

The use of galvanostatic conditions enables a good Ni metal deposit to be obtained, while potentiostatic conditions result in an almost complete depletion of nickel in the electrolyte.
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1. Introduction

Today lithium and lithium-ion batteries represent about 28% of the rechargeable battery world market and their use is increasing, particularly in small rechargeable cells for the four c sectors: cellular, computers, videocameras and cordless. In the last five years, the Li-ion and -polymer cells market has increased, from 8.4% to 27.3%, while the Ni–Cd batteries decreased from 63.8% to 44.4% and Ni–MH remained practically constant (Braun, 1996). Furthermore, it must be considered that industrial and electric vehicles applications are gaining growing attention (Rand et al., 1998).

In the future, the recycling of these batteries will be very important, both from an environmental and an economic point of view. In fact, for the battery industries it could be very interesting to recover battery materials to recycle in the production of new ones.

At the moment, $LiCoO_2$ is the most used active cathodic material, however, the use of $LiCo_xNi_{1-x}O_2$ has increased in the last few years (Broussely et al., 1999; Cho et al., 2000). The stoichiometry of the complex oxide considers x included between 0 and 1 (with preference for Ni contents above about 70%), thus the dissolution of the active cathodic material gives a solution containing both cobalt and nickel in variable concentrations.

The separation and recovery of the two metals cannot be achieved by direct electrochemical methods, due to the anomalous co-deposition that is characterised by the fact that the thermodynamically more noble metal deposits after the more electronegative one (Sasaky and Talbot, 2000; Goméz et al., 1999; Goméz and Vallés, 1995; Harris and Massey, 1998; Lupi and Pilone, 2001). In Ni–Co electrodeposited binary alloys the Co content can be much higher than in the electrolyte, though the standard electrode potentials of Ni/Ni^{2+} and Co/Co^{2+} are -0.250 and -0.277 V vs. SHE respectively (Brenner, 1963). Thus it is necessary to separate Co from Ni in advance.

The very similar chemical and physical properties of the two metals make their separation extremely difficult, but the use of Cyanex 272 as the extractant in solvent extraction seems to overcome this problem. The increase of cobalt–nickel separation factor has been reported to be a function of several parameters such as: the temperature of the process and the O/A ratio (Flett, 1987;

Preston, 1982; Cox and Flett, 1987), the aromaticity of the organic diluent (Preston, 1982; Orive et al., 1992), presence of impurities in the aqueous solution (Senapati et al., 1994) and the ionic strength of the aqueous solution (Sole and Hiskey, 1992). The Co–Ni separation has been improved by using phosphorus based acidic extractants saponified with Na(OH) (Devi et al., 1994, 1998) or aqueous ammonia (Lindell et al., 2000).

When considering nickel electrowinning, one of the problems related to the metal deposition from the sulphate solution is the competing hydrogen reduction reaction. This reaction can cause a current efficiency decrease, as well as deposit curling and cracking due to internal stresses and hydrogen incorporation (Holm and O'Keefe, 2000). To avoid these problems, boric acid and ammonium sulphate, principally as buffer, were added to the solution. In particular, boric acid appeared to act not only as a buffer (Yin and Lin, 1996), but also as a precursor of a weak nickel borate complex which catalyses the nickel deposition reaction (Ji et al., 1995).

This work aims at recovering Ni metal of high purity, by electrowinning after preventive separation by solvent extraction of Co from Ni. In particular, studies have been performed using both galvanostatic and potentiostatic methods: the former was used to obtain a good Ni metal deposit, and the latter to provide a nickel depletion in the electrolyte.

2. Experimental

The electrowinning tests were made using both Ni synthetic solutions and solutions prepared by dissolving the cathode material of Li-ion exhausted batteries with H_2SO_4 and H_2O_2 pure reagents in an appropriate ratio (Pasquali and Lupi, 2001). The last solution was used after Ni–Co separation by solvent extraction methods. The aqueous raffinate was utilised after active carbon treatment as an electrolyte in galvanostatic operations (Ni concentration higher than 40 g/l), while in potentiostatic conditions it was diluted to have a Ni content equal to 1.7–1.8 g/l. Potentiostatic electrodeposition needs an ammoniacal solution in order to obtain the best yield, thus the sulphuric solution was neutralised and added with ammonia to obtain an ammoniacal buffer.

Galvanostatic apparatus: The electrowinning tests were performed at a current density of 125–250 A/m^2, using an Amel galvanostat, an Amel coulommeter and a Linseis recorder. A 1000 cm^3 metacrylate cell was equipped with an aluminium or stainless steel cathode and a Pb–8Sb anode, spaced 3 cm apart. A polypropylene membrane separated the cathodic and anodic compartments. The initial pH adjustment and the discontinuous catholyte pH correction were made using H_2SO_4 and KOH solutions. Boric acid, which played the

role of buffer substance, was added to the catholyte. The temperature was kept constant at the prefixed value using a JULABO thermostat. The electrolysis tests lasted 2 h: shorter test duration was caused by early deposit detachment from cathode, or breaking caused by relevant internal stresses.

Potentiostatic apparatus: The potentiostatic electrolysis tests were carried out using an EG&G PAR potentiostat at constant potential (−1.20 to −1.50 V vs. SCE) and at room temperature. The potentiostat was connected to a computer for data acquisition and analysis. In the electrolytic cell, the anodic and cathodic compartments, 200 ml each, were separated by a BDH anionic exchange membrane. The cathode consisted of aluminium net or foil and the anode was titanium net.

The *quantitative* analysis of Ni and Co in the aqueous solutions was obtained by Atomic Absorption Spectroscopy (UNICAM 969). The pH solutions were monitored using an Amel pH-meter. The Ni deposits were observed and analysed by SEM (Hitachi S2500 and Philips 505, the former was equipped with EDS KEVEX apparatus for quantitative analysis). The X-ray analyses were performed using a Philips PW 1390 diffractometer.

3. Results and discussion

3.1. Ni–Co separation by solvent extraction

Cobalt anomalous co-deposition, in the presence of nickel, hinders the selective recovery of the two metals by electrowinning. Thus, recovering nickel from Li-ion cathodic past dissolution needs a previous Ni–Co separation.

Following the results obtained in previous work (Lupi et al., 1999), the separation of Ni from Co was performed by solvent extraction, with saponified 0.5 M CYANEX 272 in kerosene. The saponification agent was a 5 M KOH solution added to the organic phase in a quantity equal to 4% by volume. It can be seen in Table 1 that the organic saponification improves the separation factor between Co and Ni 100 times if added in a quantity equal to 2%, and about 500 times if the addition is 4%.

By using an *O/A* ratio equal to 3 with three stages it is possible to leave few ppm of Co in the aqueous raffinate.

Table 1
Influence of saponification on the separation factor between Co and Ni, working at pH 4.6

KOH added (vol.%)	β(Co/Ni)
0	2.32
2	242.16
4	1180.37

After treatment with active carbon, the raffinate produced has been used as an electrolyte.

3.2. Galvanostatic Ni recovery

In order to choose the best cathode material, preliminary electrowinning experiments were carried out on synthetic solutions containing about 50 g/l Ni. Titanium, aluminium and AISI 316L cathodes were tested over a temperature range of 25–50 °C, at a catholyte pH of 4.2. The deposits obtained on the Ti cathode at any temperature were characterised by internal stresses, and they broke off from the titanium surface quite rapidly. Analogous results were obtained with the aluminium cathode. Better results were obtained using AISI 316L as the cathode, although, once again, the deposits tended to break off after 1 h of electrowinning.

On the grounds of these results, the AISI 316L cathode was selected for the galvanostatic tests reported in this work. The more representative tests are summarised in Table 2. The results show the influence of process parameters, such as temperature, catholyte pH, current density and the presence of boric acid in solution, on current efficiency, cell voltage and specific energy consumption.
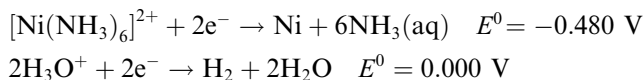
Comparing the results shown in Table 2, it can be seen that temperature has a great effect on deposition time. It should be noted that the duration of the tests was fixed at 2 h; shorter test durations were caused by the early detachment of the deposit from the cathodic support, or breaking caused by relevant internal stresses. The influence of pH is more effective at lower current densities. The addition of boric acid doubles the time before deposit detachment, maintaining almost the same results in terms of current efficiency and cell voltage. The use of boric acid is important, as it acts as a buffer and improves deposit morphology. Indeed, considering tests performed without buffer, as the pH correction is discontinuous, the local pH increases when KOH is added, so producing hydroxide precipitation and its incorporation in the cathodic deposit.

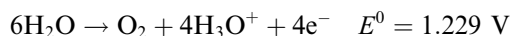The deposit morphology does not show remarkable changes in the presence of boric acid, as highlighted in Fig. 1. In both cases the deposit looks compact and homogenous, with rounded particles.

3.3. Potentiostatic Ni recovery

The reactions occurring at the cathode surface suggest the choice of the electrode material. The possible cathodic reactions are:

$$[\text{Ni(NH}_3)_6]^{2+} + 2e^- \rightarrow \text{Ni} + 6\text{NH}_3(\text{aq}) \quad E^0 = -0.480 \text{ V}$$

$$2\text{H}_3\text{O}^+ + 2e^- \rightarrow \text{H}_2 + 2\text{H}_2\text{O} \quad E^0 = 0.000 \text{ V}$$

while the anodic reaction is

$$6\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}_3\text{O}^+ + 4e^- \quad E^0 = 1.229 \text{ V}$$

Preliminary cyclic voltammetry tests carried out on different cathode materials (platinum, nickel and aluminum) show that the Al cathode has the best characteristics for Ni deposition in terms of hydrogen overvoltage.

The cyclic voltammetry performed with the Al cathode using both the blank (Fig. 2a) and the Ni containing solution (Fig. 2b), shows that Ni electrodeposition starts at about −800 mV vs. SCE, before hydrogen evolution. A test performed at −1.0 V required long times for the complete depletion of nickel. The best results, in terms of deposit quality and electrolysis time, are reached by working at −1.5 V vs. SCE.

Indeed, after 80 min the solution that was dark blue initially became colourless, and a thick grey Ni powder covered the Al net cathode. Fig. 3 shows a typical current–time curve for Ni potentiostatic deposition at −1.5 V vs. SCE. The current initially increases rapidly because of Ni deposition and then decreases due to the Ni depletion. The nickel left in the electrolyte is about 100 ppm.

The yield of the process can be calculated by drawing samples at fixed times. In Table 3 the Ni content of samples was drawn every 10 min, Δ (ppm), the coulombs calculated and experimental are reported together with current efficiency. It can be seen that after 80 min the nickel concentration is 84 ppm and the current efficiency

Table 2
Results of nickel electrowinning with the AISI 316L cathode, using a solution containing 49.5 g/l Ni

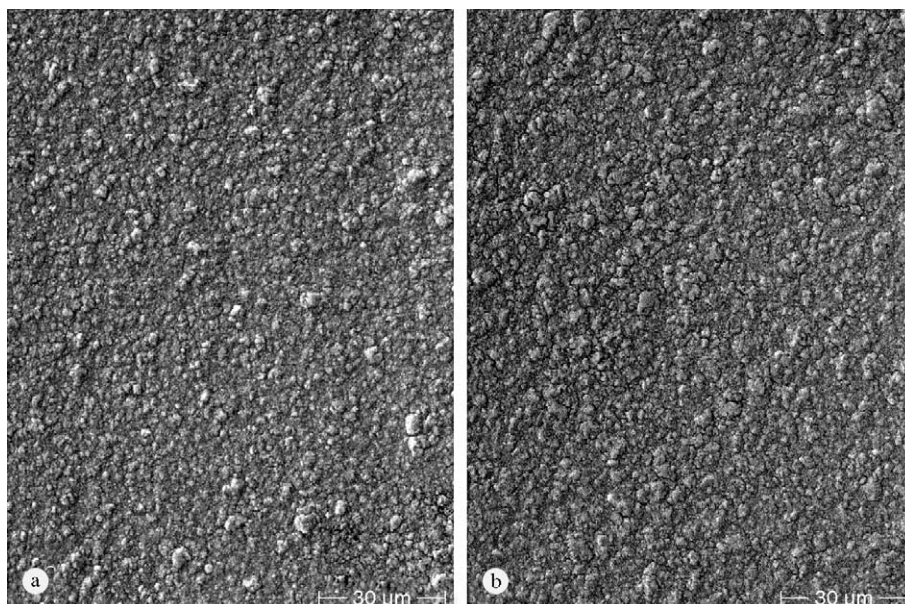| Time (h)	H_3BO_3 (g/l)	Catholyte pH	CD (A/m^2)	T (°C)	η_I (%)	ΔV (V)	Spec. energy consumption (kW h/kg)
0.50	–	4.2	125	25	88.21	2.810	2.91
1.40	–	3.2	125	40	84.11	2.630	2.86
0.84	–	3.2	250	40	89.43	2.936	3.00
0.90	–	4.2	250	40	92.64	3.035	2.99
1.22	20	3.2	250	25	89.83	3.124	3.18
1.70	20	3.2	250	40	88.22	2.986	3.09
2.00	20	3.2	250	50	86.91	2.820	2.96

Fig. 1. SEM micrographs of Ni deposit obtained without (a) and with (b) boric acid addition.
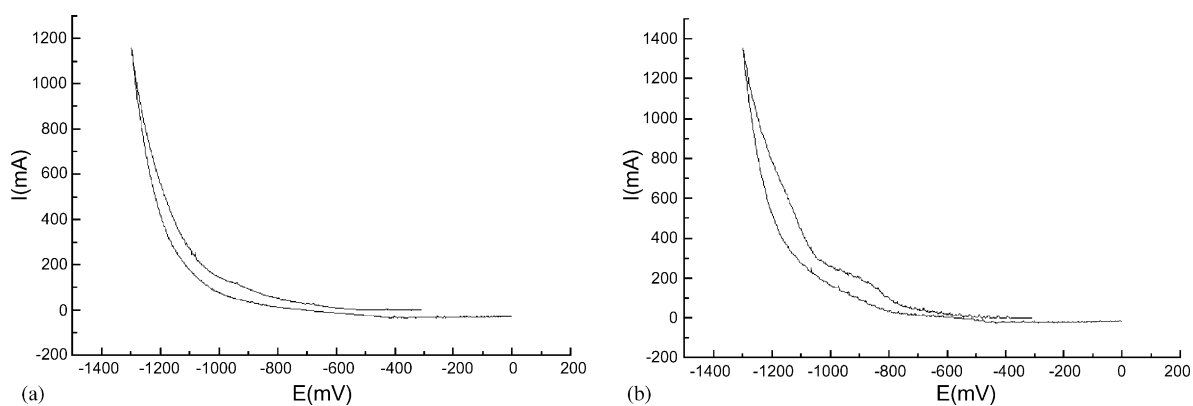

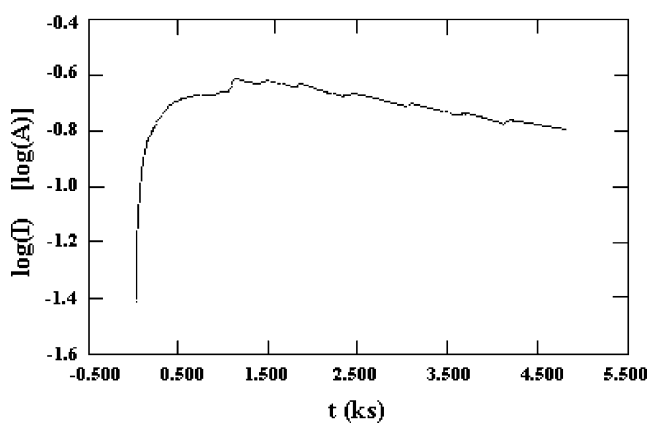Fig. 2. Cyclic voltammetry on the blank solution (a) and on the Ni containing solution (b).

Fig. 3. Current–time curve for Ni potentiostatic deposition from a solution containing 1.74 g/l Ni.

is about 45%; this value is acceptable considering the very low Ni content.

Tests carried out at above room temperature do not give better results in terms of both deposit morphology and current efficiency.

The X-ray analysis confirmed that the produced powder was metallic Ni as shown in Fig. 4; the 2θ values fit with those reported in the literature (01-1260 of Power Diffraction File). The space group is *Fm3m*.

The deposit morphology is shown in Fig. 5, where a characteristic dendritic structure is visible, this represents the starting point for globular nickel growing. The Ni deposit is not compact and consists of a powder that can be easily recovered from the aluminium electrode.

4. Conclusions

A hydrometallurgical process to recycle Li-ion and -polymer batteries with $LiCo_xNi_{(1-x)}O_2$ as a cathode

Table 3
Results of the test carried out at −1.5 V SCE

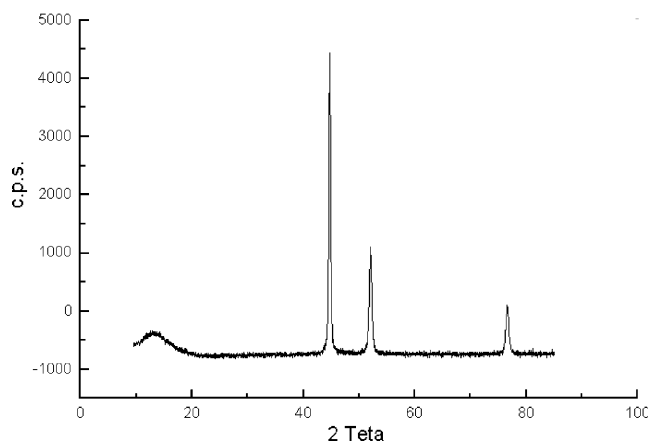| Time (min)	ppm	Δ (ppm)	Qc (C)	Qr (C)	η (%)
0	1740	–	–	–	–
10	1330	410	135	200	67.4
20	972	768	253	383	65.9
30	697	1043	343	577	59.4
40	453	1287	423	745	56.8
50	335	1405	462	895	51.6
60	299	1441	474	1014	46.7
70	138	1596	525	1109	47.3
80	84	1656	545	1206	45.1

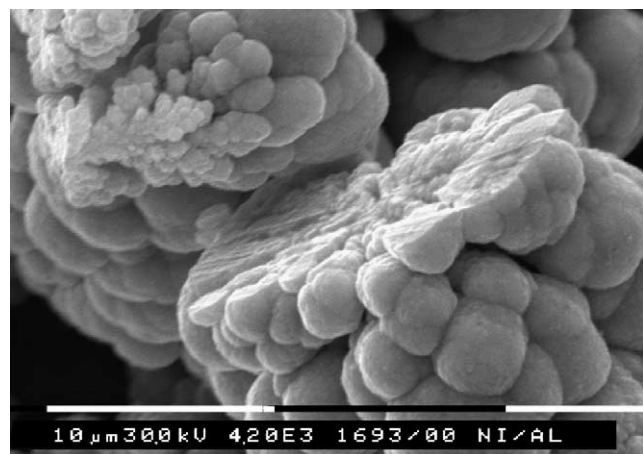Fig. 4. X-ray analysis of the Ni powder electrowon at constant potential.

Fig. 5. SEM micrograph of Ni deposit obtained with potentiostatic method.

has been investigated. The operations involved in this process are: cathodic paste leaching, cobalt–nickel separation by solvent extraction, Ni metal recovery by electrowinning at constant current density, and Ni powder recovery by electrolysis at constant potential, carried out on a partially depleted electrolyte.

Solvent extraction with modified Cyanex 272 in kerosene has been used to separate Co from Ni. The resulting raffinate does not practically contain Co, resulting in a good electrolyte for Ni production after treatment with active carbon.

Nickel electrowinning performed at 250 A/m^2 current density, 50 °C temperature, pH = 3–3.2, with an electrolyte having about 50 g/l Ni and 20 g/l H_3BO_3 composition, produces a good aspect Ni deposit with a current efficiency and a specific energy consumption of about 87% and 2.96 kW h/kg respectively.

The electrolysis at constant potential of a solution containing 1.7–1.8 g/l of Ni produces a very pure powder in 80 min, leaving less than 100 ppm of nickel in solution.

Acknowledgement

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